Claims

1. A proton conducting membrane comprising a support filled with a proton conducting structure (β) comprising an acid-containing structure containing an acid group, the support comprising an organic-inorganic composite structure (α) having a crosslinked structure formed by a metal-oxygen bond and an open-cell structure having internally-formed pores connected continuously to each other by said crosslinked structure.

2. The proton conducting membrane as described in Claim 1, wherein the ratio of the number of metallic atoms to carbon atoms in the organic-inorganic composite structure (α) falls within a range of from 2 : 1 to 1 : 25.

3. The proton conducting membrane as described in Claim 1 or 2, wherein the metallic atom in the organic-inorganic composite structure (α) is silicon atom.

4. The proton conducting membrane as described in any one of Claims 1 to 3, wherein the porosity of the open-cell structure falls within a range of from 20 to 95% by volume based on the support comprising the organic-inorganic composite structure (α).

5. The proton conducting membrane as described in any one of Claims 1 to 4, wherein a diameter of the pores is from 0.01 to 10 μm.

6. The proton conducting membrane as described in any one of Claims 1 to 5, wherein the organic-inorganic composite structure (α) comprises at least a structure represented by the following formula (1):

$$X_{3-n_1} — \underset{\displaystyle (R^2)_{n_1}}{\overset{}{M}} — R^1 — \underset{\displaystyle (R^2)_{n_2}}{\overset{}{M}} — X_{3-n_2} \quad \cdots (1)$$

wherein M represents a silicon atom; X represents -O-bond taking part in crosslinking or OH group; R^1 represents a C_1–C_{50} carbon atom-containing molecular chain; R^2 represents a methyl, ethyl, propyl or phenyl group; and n1 and n2 each represent 0, 1 or 2, with the proviso that at least one of n1 and n2 represents 1 or 2.

7. The proton conducting membrane as described in Claim 6, wherein the number of the groups X taking part in the crosslinking of the organic-inorganic composite structure (α) represented by the chemical formula (1) is represented by the following numerical formula (II):

$$\sum_{i=1}^{P} m_i\{6-(n_1^i+n_2^i)\}=a$$

$$a: 2.9<a<3.5 \quad \ldots (II)$$

wherein P is the number of the kinds of the compound corresponding to the chemical formula (1) contained in the organic-inorganic composite structure (α) which is an integer of 1 or more; i represents an integer of from 1 to P; $n1^i$ and $n2^i$ represent n1 and n2 in the formula (1) in the organic-inorganic composite structure (α)i, respectively, which each are 0, 1 or 2, with the proviso that at least one of $n1^i$ and $n2^i$ is 1 or 2; and m_i represents a molar fraction.

8. The proton conducting membrane as described in Claim 7, wherein a in the numerical formula (II) is 3.0.

9. The proton conducting membrane as described in any one of Claims 1 to 8, wherein the proton conducting structure (β) has

a crosslinked structure formed by metal-oxygen atom and comprises an acid group-containing structure (A) represented by the following formula (3):

$$X_{3-m}\text{—}\underset{\underset{(R^4)_m}{|}}{M}\text{—}R^3 \qquad \cdots (3)$$

wherein M represents a silicon atom; X represents -O-bond taking part in crosslinking or OH group; R^3 represents a molecular chain having at least one acid group; R^4 represents any of methyl, ethyl, propyl and phenyl groups; and m represents 0, 1 or 2.

10. The proton conducting membrane as described in Claim 9, wherein R^3 in the formula (3) is a structure represented by the following formula (12):

$-(CH_2)_n-SO_3H$ (12)

wherein n represents an integer of from 1 to 20.

11. The proton conducting membrane as described in Claim 9, wherein the proton conducting structure (β) comprises a metal-oxygen bond structure (B) connected to the structure of the formula (3) by a metal-oxygen bond besides the acid group-containing structure represented by the formula (3).

12. The proton conducting membrane as described in Claim 11, wherein the metal-oxygen bond structure (B) comprises an organic-inorganic composite structure (2) represented by the following formula:

$$X_{3-n_1}\text{—}\underset{\underset{(R^2)_{n_1}}{|}}{M}\text{—}R^1\text{—}\underset{\underset{(R^2)_{n_2}}{|}}{M}\text{—}X_{3-n_2} \qquad \cdots (2)$$

wherein M represents a silicon atom; X represents -O-bond taking part in crosslinking or OH group; R^1 represents a C_1-C_{50} carbon atom-containing molecular chain; R^2 represents any of methyl, ethyl, propyl and phenyl groups; and n1 and n2 each represent 0, 1 or 2.

13. The proton conducting membrane as described in Claim 11, wherein the metal-oxygen bond structure (B) comprises a structure represented by the following formula (6):

$$M(R^2)_m(X)_{4-m} \qquad (6)$$

wherein M represents a metallic atom; X represents -O-bond taking part in crosslinking or OH group; R^2 represents any of methyl, ethyl, propyl and phenyl groups; and m represents 0, 1 or 2.

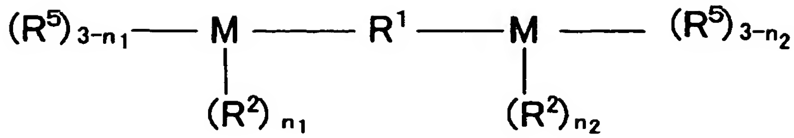
14. The proton conducting membrane as described in Claim 13, wherein M in the formula (6) is a silicon atom.

15. The proton conducting membrane as described in Claim 13, wherein m in the formula (6) is 0.

16. A method of producing a proton conducting membrane as described in Claim 1, wherein the organic-inorganic composite structure (α) is produced by a method comprising a step of preparing a mixture containing an organic-inorganic composite crosslinkable compound (C) terminated by a crosslinkable silyl group and a carbon group covalently connected thereto, a step of forming said mixture into a film and a step of subjecting the crosslinkable silyl group contained in the mixture thus film-formed to hydrolysis and/or condensation.

17. The method of producing a proton conducting membrane as described in Claim 16, wherein the organic-inorganic composite crosslinkable compound (C) is represented by the following formula

(4):



... (4)

wherein M represents a silicon atom; R^1 represents a C_1-C_{50} carbon atom-containing molecular chain; R^2 represents any of methyl, ethyl, propyl and phenyl groups; R^5 represents any of Cl, OH, OCH_3, OC_2H_5, OC_3H_7, OC_4H_9, OC_6H_5 and $OCOCH_3$; and n1 and n2 each represent 0, 1 or 2, with the proviso that at least one of n1 and n2 is 1 or 2.

18. The method of producing a proton conducting membrane as described in Claim 17, wherein the number of hydrolyzable groups in the organic-inorganic composite crosslinkable compound (C) represented by the formula (4) is represented by the following numerical formula (II):

$$\sum_{i=1}^{P} m_i\{6-(n_1^i+n_2^i)\}=a \qquad a:\ 2.9<a<3.5 \quad \ldots \text{ (II)}$$

wherein P is the number of the kinds of the organic-inorganic composite crosslinkable compound (C) which is an integer of 1 or more; i represents an integer of from 1 to P; $n1^i$ and $n2^i$ represent n1 and n2 in the formula (4) in the organic-inorganic composite crosslinkable compound (C)i, respectively, which each are 0, 1 or 2, with the proviso that at least one of $n1^i$ and $n2^i$ is 1 or 2; and m_i represents a molar fraction.

19. The method of producing a proton conducting membrane as described in Claim 18, wherein a in the numerical formula (II) is 3.0.

20. The method of producing a proton conducting membrane as

described in Claim 16, further comprising a step of adding a catalyst in an amount arranged such that water is present in an amount of from 0.5 to 1.5 equivalents to the crosslinkable silyl group in the organic-inorganic composite crosslinkable compound (C).

21. The method of producing a proton conducting membrane as described in Claim 16, wherein a Brønsted acid is used as a catalyst during the hydrolysis of the crosslinkable silyl group in the organic-inorganic composite crosslinkable compound (C).

22. The method of producing a proton conducting membrane as described in Claim 16, further comprising a step of mixing the organic-inorganic composite crosslinkable compound (C) with a solvent in an amount of from 0.5 to 10 ml per g of the solid content of the organic-inorganic composite crosslinkable compound (C).

23. A method of producing a proton conducting membrane as described in Claim 1, wherein the proton conducting membrane is produced by a method comprising a step of filling the organic-inorganic composite structure (α) with a mixture comprising an acid group-containing compound (D) containing at least a crosslinkable silyl group and an acid group and then subjecting the crosslinkable silyl group contained in the mixture which has thus filled the structure (α) to hydrolysis and/or condensation to form a crosslinked structure of proton conducting structure (β) inside the organic-inorganic composite structure (α).

24. The method of producing a proton conducting membrane as described in Claim 23, wherein the acid group-containing compound (D) has a structure represented by the following formula (7):

$$(R^6)_{3-m}-\underset{\underset{(R^4)_m}{|}}{Si}-R^3 \qquad (7)$$

wherein R^6 represents any of OH, OCH_3, OC_2H_5 and OC_3H_7; R^3 represents a molecular chain having at least one acid group; R^4 represents any of methyl, ethyl, propyl and phenyl groups; and m represents 0, 1 or 2.

25. The method of producing a proton conducting membrane as described in Claim 23, wherein the acid group-containing compound (D) comprises one having a structure represented by the following formula (8):

$$(R^7)\!\left(O-\overset{\overset{R^3}{|}}{\underset{\underset{R^8}{|}}{Si}}\right)_n\!\left(O-\overset{\overset{R^9}{|}}{\underset{\underset{R^{10}}{|}}{Si}}\right)_t\!-R^{11} \qquad (8)$$

wherein R^3 represents a molecular chain having at least one acid group; R^7 represents a group selected from the group consisting of H, CH_3, C_2H_5, C_3H_7, C_4H_9 and C_6H_5 which may have a branched structure that partly constitutes -Si bond or an intramolecular annular structure; R^8, R^9, R^{10} and R^{11} each represent a group selected from the group consisting of R^3, OH, OCH_3, OC_2H_5, OC_3H_7, OC_4H_9, OC_6H_5, CH_3, C_2H_5, C_3H_7, C_4H_9 and C_6H_5 that partly constitutes -OSi bond or an intramolecular annular structure; n represents an integer of from 1 to 50; t represents an integer of from 0 to 50, with the proviso that the sum of n and t is not greater than 100; and the compound may be a combination of compounds wherein n and t are the same or different.

26. The method of producing a proton conducting membrane as described in Claim 24 or 25, wherein R^3 in the formula (7) or (8) is a structure represented by the following formula (12):

$$-(CH_2)_n-SO_3H \qquad (12)$$

wherein n represents an integer of from 1 to 20.

27. The method of producing a proton conducting membrane as described in any one of Claims 23 to 26, wherein the mixture filling the organic-inorganic composite structure (α) comprises a crosslinkable compound (F) represented by the following formula (16) besides the acid group-containing compound (D) containing a crosslikable silyl group and an acid group:

$$M(R^2)_m(R^5)_{4-m} \qquad (16)$$

wherein M represents a metallic atom; R^5 represents any of OH, OCH_3, OC_2H_5, OC_3H_7, OC_4H_9, OC_6H_5, Cl and $OCOCH_3$; R^2 represents any of methyl, ethyl, propyl and phenyl groups; and m represents 0, 1 or 2.

28. A method of producing a proton conducting membrane, wherein the proton conducting membrane (β) described in Claim 1 is produced by a method comprising a step of filling the organic-inorganic composite structure (α) with a mixture comprising an acid group precursor-containing compound (E) containing at least a crosslinkable silyl group and an acid precursor group capable of being converted to an acid group and then subjecting the crosslinkable silyl group contained in the mixture which has thus filled the structure (α) to hydrolysis and/or condensation to form a crosslinked structure and a step of subjecting the acid group precursor in the acid group precursor-containing compound (E) to oxidation and/or hydrolysis to produce an acid group, thereby

forming a proton conducting structure (β) having an acid group inside the organic-inorganic composite structure (α).

29. The method of producing a proton conducting membrane as described in Claim 28, wherein the acid group precursor-containing compound (E) has a structure represented by the following formula (17):

$$\begin{array}{c} (R^{12})_{3-m}-\underset{\displaystyle (R^{4})_{m}}{\underset{|}{Si}}-R^{13} \end{array} \qquad (17)$$

wherein R^{12} represents any of OH, OCH_3, OC_2H_5 and OC_3H_7; R^{13} represents a molecular chain having at least one acid group precursor; R^4 represents any of methyl, ethyl, propyl and phenyl groups; and m represents 0, 1 or 2.

30. A method of producing a proton conducting membrane as described in Claim 28, wherein the acid group precursor-containing compound (E) has a structure represented by the following chemical formula (13):

$$(R^7)\!\!-\!\!\left(O-\overset{\displaystyle R^{13}}{\underset{\displaystyle R^{8}}{Si}}\right)_{n}\!\!-\!\!\left(O-\overset{\displaystyle R^{9}}{\underset{\displaystyle R^{10}}{Si}}\right)_{t}\!\!-R^{11} \qquad (13)$$

wherein R^{13} represents a molecular chain having at least one acid group precursor; R^7 represents a group selected from the group consisting of H, CH_3, C_2H_5, C_3H_7, C_4H_9 and C_6H_5 which may have a branched structure that partly constitutes -Si bond or an intramolecular annular structure; R^8, R^9, R^{10} and R^{11} each represent a group selected from the group consisting of R^{13}, OH, OCH_3, OC_2H_5, OC_3H_7, OC_4H_9, OC_6H_5,

CH_3, C_2H_5, C_3H_7, C_4H_9 and C_6H_5 that partly constitutes -OSi bond or an intramolecular annular structure; n represents an integer of from 1 to 50; t represents an integer of from 0 to 50, with the proviso that the sum of n and t is not greater than 100; and the compound may be a combination of compounds wherein n and t are the same or different.

31. The method of producing a proton conducting membrane as described in Claim 29 or 30, wherein R^3 in the formula (16) or (13) is a structure represented by the following formula (15):

$$-(CH_2)_n-SH \qquad (15)$$

wherein n represents an integer of from 1 to 20.

32. The method of producing a proton conducting membrane as described in any one of Claims 28 to 31, wherein the proton conducting structure (β) filling the organic-inorganic composite structure (α) comprises a crosslinkable compound (F) represented by the following formula (14) besides the acid group precursor-containing compound (E):

$$M(R^2)_m(R^6)_{4-m} \qquad (14)$$

wherein M represents a metallic atom; R^6 represents any of OH, OCH_3, OC_2H_5, OC_3H_7, OC_4H_9, OC_6H_5, Cl and $OCOCH_3$; R^2 represents any of methyl, ethyl, propyl and phenyl groups; and m represents 0, 1 or 2.

33. A fuel cell comprising a proton conducting membrane as described in any one of Claims 1 to 15.